

365-428PCT

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/402674
NEW

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

| | | |
|-------------------------------|---------------------------|-----------------------|
| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |
| PCT/FI98/00329✓ | 14 April 1998✓ | 11 April 1997✓ |

TITLE OF INVENTION

POLYOL AND COMPLEX ESTERS FOR USE WITH, IN PARTICULAR, FLUORINATED REFRIGERANTS✓

APPLICANT(S) FOR DO/EO/US

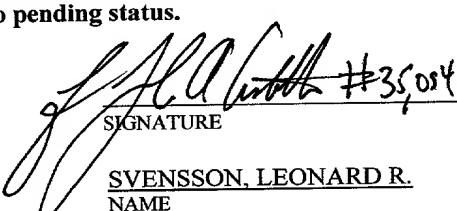
KOISTINEN, Jari; RISSANEN, Kari; SILVENNOINEN, Laura; KOSKIMIES, Salme ✓

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau). (appln. encl. W098/46706)
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. A translation of the International Application into English (35 U.S.C. 371(c)(3)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)).
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.97 and 1.98. International Search Report
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A FIRST preliminary amendment.
 A SECOND or SUBSEQUENT preliminary amendment.
14. A substitute specification.
15. A change of power of attorney and/or address letter.
16. Other items or information:
 - 1.) PCT Request (PCT/RO/101)
 - 2.) International Search Report (PCT/IPEA/409) w/Amended Claims
 - 3.) Zero (0) Sheet of Formal Drawing

| | | | | |
|--|--------------|----------------------------------|--------------------------|-----------|
| U.S. APPLICATION NO. (if known, see 37 CFR 1.5) | | INTERNATIONAL APPLICATION NO | ATTORNEY'S DOCKET NUMBER | |
| 08y 402674 | | PCT/FI98/00329 | 365-428PCT | |
| 17. <input checked="" type="checkbox"/> The following fees are submitted: | | CALCULATIONS PTO USE ONLY | | |
| BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5): | | | | |
| Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... | | \$970.00 | | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO | | \$840.00 | | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... | | \$760.00 | | |
| International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) | | \$670.00 | | |
| International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). | | \$96.00 | | |
| ENTER APPROPRIATE BASIC FEE AMOUNT = | | \$ 970.00 | | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | \$ | | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | |
| Total Claims | 23 - 20 = | 3 | X \$18.00 | \$ 54.00 |
| Independent Claims | 3 - 3 = | ----- | X \$78.00 | \$ ----- |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | Yes | + \$260.00 | \$ 260.00 |
| TOTAL OF ABOVE CALCULATIONS = | | \$ 1284.00 | | |
| Reduction of ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28). | | \$ | | |
| SUBTOTAL = | | \$ 1284.00 | | |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | \$ | | |
| TOTAL NATIONAL FEE = | | \$ 1284.00 | | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | \$ 40.00 | | |
| TOTAL FEES ENCLOSED = | | \$ 1324.00 | | |
| | | Amount to be: refunded | \$ | |
| | | charged | \$ | |
| <p>a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1324.00</u> to cover the above fees is enclosed.</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-2448</u>.</p> | | | | |
| <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> | | | | |
| <p>Send all correspondence to: Birch, Stewart, Kolasch & Birch, LLP P.O. Box 747 Falls Church, VA 22040-0747 (703)205-8000</p> | | | | |
|  SIGNATURE SVENSSON, LEONARD R. NAME #30,330 REGISTRATION NUMBER | | | | |
| <small>/LRS/sas October 8, 1999</small> | | | | |

09/402674
514 Rec'd PCT/PTO 08 OCT 1999

PATENT
365-428PCT

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: KOISTINEN, Jari et al
Int'l. Appl. No.: PCT/FI98/00329
Appl. No.: New Group: Unknown
Filed: October 8, 1999 Examiner: UNKNOWN
For: POLYOL AND COMPLEX ESTERS FOR USE
WITH, IN PARTICULAR, FLUORINATED
REFERIGERANTS

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

October 8, 1999

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/FI98/00329 which has an International filing date of April 14, 1998, which designated the United States of America.--

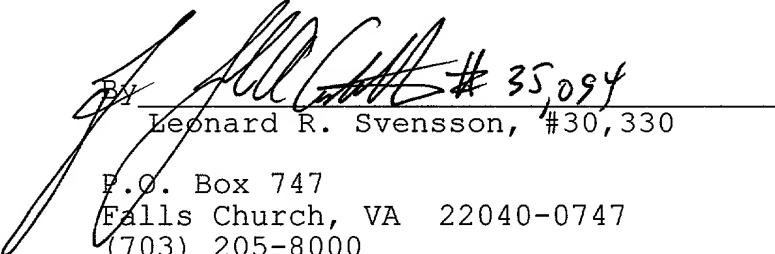
REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP


By _____ # 35,094
Leonard R. Svensson, #30,330

P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

LRS/sas
365-428PCT

(Rev. 03/30/99)

514 Rec'd PCT/PTO 08 OCT 1999

Polyol and complex esters for use with, in particular, fluorinated refrigerants

The present invention concerns a refrigerant compositions according to the preambles of claims 1, 3, 5 and 7. Compositions of this kind generally contain a non-chlorinated hydrofluorocarbon based refrigerant composition together with a polyol ester based lubricant mixed therewith.

The invention also concerns complex esters according to claim 16 and the use thereof in lubricants.

10

Lately, as a result of development in many fields of application, the evolution of polyolester type lubricants has been rapid. These products can be used as such or mixed with another base oil, such as a hydrocarbon, in engine oils for automotives, in aeroplane and gas turbine oils, as biodegradable hydraulic oils, as metal working oils and as compressor oils. These products are used in particular together with fluorinated refrigerants as a soluble lubricant component in refrigeration compressors due to their advantageous solubility properties, good technical stability and good cold properties.

15

The use of, e.g., neopentylglycol and pentaerytritol esters together with refrigerants has been generally suggested. Although these known esters in principle exhibit good lubricant properties, their solubility in non-chlorinated hydrofluorocarbons is often only fair. For this reason they do not work well enough in refrigerant compositions containing fluorinated hydrocarbons.

20

It is an object of the present invention to eliminate the problems of the prior art and to provide polyol and complex esters of a novel kind which can be used in particular together with fluorinated refrigerant liquids as lubricants. It is another object of the invention to provide novel esters which are generally suited to the use as base oils of lubricants.

25

The present invention is based on the finding that polyol or complex esters of 3-hydroxy-2,2-methyl-3-hydroxy-2,2-dimethylpropionate, i.e. hydroxypivalyl hydroxypivalate, which have good lubricant properties, also exhibit a good or excellent solubility in fluorinated refrigerants and they are therefore suitable for use in refrigerant compositions containing this kind of refrigerants. In particular the polyol esters used comprise the polyol HPHP

30

(hydroxypivalyl hydroxypivalate) as such or together with another polyol, such as NPG, BEPD, ETHD, TMP, TME or PE and the carboxylic acid is a linear or branched C₅ - C₁₈

monocarboxylic acid or a hydroxy acid, such as hydroxypivalic acid or a mixture of mono- and dicarboxylic acids, such as adipic acid, sebasic acid, azelaic acid, dimethylmalonic acid or cyclic anhydrides.

5 More specifically, the refrigerant composition according to the present invention is mainly characterized by what is stated in the characterizing parts of claims 1, 3, 5 and 7.

Complex esters of HPHP are novel and useful as base oils of lubricant oils. The novel esters are characterized by what is stated in the characterizing part of claim 16.

10 The present invention provides considerable advantages. Thus, as mentioned above, the esters of HPHP have good lubricant properties and good solubility in HFC compounds used as refrigerants. The raw materials of said oils can be produced by the economically advantageous oxo-process (hydroformulation). The properties of the oils can easily be modified depending on the application by varying the ratio of the polyols of the ester (the amount of HPHP can be 100 to 5 mol-% of the total amount of polyol), the esterifying carboxylic acid and/or the ratio between the esterifying carboxylic acids. By using branched acids the solubility can be improved and by using dibasic acids the viscosity can be raised.

20 In the following, the invention will be examined with the aid of a detailed description and using a number of working examples.

25 The present esters comprise polyol or complex esters of 3-hydroxy-2,2-methyl-3-hydroxy-2,2-dimethylpropionate. "Polyol ester" means i.a. esters having a carboxylic group comprising a monobasic acid or an anhydride thereof. For the purpose of the present invention, the term "polyol ester" comprises generally also "complex esters" which are esters in which at least a part of the esterifying acids are dibasic. Usually both carboxylic groups of these acids react with an alcohol and yield oligomeric ester compounds, which 30 contain at least two alcohol residues and one carboxylic acid residue. Complex esters also include esters having the carboxylic acid residue formed by a hydroxy acid containing both a hydroxyl group and a carboxylic group. The carboxylic group reacts with the polyol, whereas the hydroxyl group reacts with the carboxylic group of another carboxylic acid.

35 "Polyol" stands for a compound with at least two hydroxy groups. According to the present invention HPHP can be esterified alone or together with another polyol. These polyols are,

e.g., NPG (neopentylglycol), BEPD (2-butyl-2-ethyl-1,3-propanediol), EHD (2-ethyl-1,3-hexanediol), TMP (trimethylol propane), TME (trimethylol ethane), PE (pentaerythritol), TMPD (2,2,4-trimethyl-pentanediol) and CHDM (1,4-dimethylol-cyclohexane). Of these polyols chemically and technically stable polyols, containing no hydrogen in the carbon in position 2 or which are (sterically) strongly hindered, such as NPG, EHD, CHDM and BEPD, are particularly preferred.

Preferably the polyol ester mixtures are formed by mixing the polyols together and by esterifying the thus formed mixture *in situ*.

- 10 According to a first preferred embodiment of the invention, a refrigerant composition is provided, comprising a polyol ester which completely or almost completely (95 mol-%, or even 100 %) consists of an ester of HPHP.
- 15 According to a second preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP an ester of TMP, TME, PE or TMPD at any ratio. Preferably HPHP forms the main part of the polyol residue of the ester mixture, i.e. its molar amount is 50 % - 100 %.
- 20 According to a third preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP a polyol ester of BEPD, the molar ratio between BEPD and HPHP being 5:95 to 99:1.
- 25 According to a fourth preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP a polyol ester of NPG, EHD or CHDM.
- 30 HPHP or a mixture of HPHP and some other polyol is esterified with a linear or branched C₄ to C₁₈ carboxylic acid or an anhydride thereof. As specific examples of aliphatic, linear or branched, saturated or unsaturated C₄-C₁₈-carboxylic acids which can be used for preparing the ester, the following can be mentioned:

- 35 I saturated, linear C₄-C₁₈-carboxylic acids: butanoic acid (butyric acid), pentanoic acid (valeric acid), hexanoic acid (caproic acid), heptanoic acid, octanoic acid (caprylic acid), decanoic acid (capric acid), dodecanoic acid (lauric acid) and hexadecanoic acid (palmitic acid) and mixtures thereof;

- II saturated, branched C₄-C₁₆-carboxylic acids: isobutanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid;
- III unsaturated, linear C₄-C₁₈-carboxylic acids: 3-butenoic acid (vinylacetic acid); and
- IV unsaturated, branched C₄-C₁₈-carboxylic acids.

5

In the mixed esters the ratios between the various linear and branched carboxylic acids can vary within large boundaries. Typically, the linear carboxylic acid(s) is (are) present in amounts of 1 to 100 mol-%, preferably about 10 to 90 mol-% of the amount of carboxylic acids. Correspondingly, the amount of branched carboxylic acids is 99 to 1 mol-%, preferably about 90 to 10 mol-%. In particular it is possible to prepare polyolesters, which contain 10 to 50 mol-% of at least one linear carboxylic acid and 90 to 50 mol-% of a branched carboxylic acid.

10

When polyol esters of HPHP are prepared it is preferred to select linear or branched acids containing 4 to 14 carbon atoms as esterifying carboxylic acid. Octanoic acid, 2-ethylhexanoic acid and lauric acid can be mentioned as examples.

15

Esterifying hydroxy acids are, e.g., hydroxypivalic acid (HPAA), lactic acid, citric acid and dimethylolepropionic acid (DMPA).

20

In addition to the afore-mentioned, the esterifying carboxylic acid used can comprise dibasic carboxylic acids, such as oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, pimelic acid, suberic acid and azelaic acid. It is also possible to use cyclic anhydrides, such as succinic anhydride or alkyl derivatives thereof, or trimellitic anhydride. Small amounts of aromatic anhydrides, such as phthalic anhydride are also possible.

25

The degree of esterification of the polyols is 50 to 100 %, preferably as high as possible, at least about 90 %. In the complex esters the ratio between the mono- and dibasic carboxylic acids is 50 : 50 to 99 : 1.

30

The polyol esters/mixed esters/complex esters of HPHP or HPHP and at least another polyol can be used for preparing refrigerant compositions. These contain as a refrigerant one or several chlorine-free hydrofluorocarbon(s) (a refrigerant) in which the ester is dissolved. As specific examples of the refrigerant liquid component of the compositions, the following can be mentioned: hydrofluorocarbon 134 (1,1,2,2-tetrafluoroethane),

35

hydrofluorocarbon 134a, hydrofluorocarbon 143 (1,1,2-trifluoroethane), hydrofluorocarbon 143a (1,1,1-trifluoroethane), hydrofluorocarbon 152 (1,2-difluoroethane) and hydrofluorocarbon 152a (1,1-difluoroethane). Of these compounds, hydrofluorocarbon 134a is generally preferred. Mixtures of hydrofluorocarbons can also be employed.

5 Examples include hydrofluorocarbon mixture 407 (mixture of hydrocarbons 32, 125 and 134a) and hydrofluorocarbon mixture 410 (mixture of hydrocarbon 32 and 125).

Depending on application, the viscosity requirement for the ester is, according to ISO-standard, between 5 and 200 cSt (40 °C). Low (5 - 10) and intermediate (22 - 32) 10 viscosities are needed for, e.g., refrigerators and other small refrigeration devices. High viscosity (46 - 68) compositions are used for, e.g., cooling equipment of air conditioners.

As already mentioned in the beginning, the viscosity of the prepared esters can be adjusted 15 as desired by suitably selecting esterifying carboxylic acid components and/or by adding a further polyol to the BEPD. Thus, by using conventional linear or branched carboxylic acids (C₄ - C₁₂) and, e.g., adipic acid, it is possible to prepare esters having viscosities in the range of about 15-22 cSt at 40 °C. Their viscosity indeces are about 100 and pour points below -40 °C. They are suitable for use in smallish cooling equipment. By increasing the amount of a branched carboxylic acid it is possible to increase the solubility 20 of the esters. By feeding a dibasic carboxylic acid into the esterification reaction and in particular by using it together with linear or branched acids, the viscosity of the product can be increased. The cold properties and good solubility remain. Mixing HPHP with another polyol before esterification makes it possible to increase even further without impairing the solubility . The viscosity increase to the range of high viscosity.

25

As examples of particularly valuable esters, the following can be mentioned:

- I Polyol esters of HPHP, which contain 30 to 60 % linear carboxylic acid and 70 to 40 mol-% branched carboxylic acid
- 30 II Complex esters of HPHP which contain 1 to 10 mol-% dibasic carboxylic acid and 90 to 99 mol-% linear and/or branched monobasic carboxylic acid; and
- III Complex esters of HPHP and NPG/BEPD, which contain 4 to 30 mol-% dibasic carboxylic acid and 96 to 70 mol-% linear and/or branched monobasic carboxylic acid.

35

As mentioned above, the complex esters of HPHP as well as complex esters of HPHP and

some other polyol, are already as such novel products which can be used in lubricant compositions for different aims. The esters work as base oil of these compositions and additives are usually employed in amounts of 0 to 20 wt.-% in the compositions for the purpose of modifying the compositions such that they are better suited for various 5 applications. Thus, the esters are suitable not only for use in refrigerant compositions but also for all applications mentioned in the introduction of the specification.

Conventional additives which can be used in the refrigerant liquid compositions include, e.g., the following: antioxidants, antiwear agents, detergents, defoaming agents and 10 corrosion inhibitors.

Suitable antioxidants include phenols, such as 2,6-di-t-butyl-4-methylphenol and 4,4'-methylene-bis(2,6-di-t-butylphenol); aromatic amines, such as p,p-dioctylphenylamine, monoocetyl diphenylamine, phenothiazine, 3,7-dioctylphenothiazine, phenyl-1-naphthylamine, phenyl-2-naphthylamine, alkylphenyl-1-naphththalamines and alkyl-phenyl-2-naphthal-amines, as well as sulphur-containing compounds, e.g. dithiophosphates, phosphites, sulphides and dithio metal salts, such as benzothiazole, tin-dialkyl dithiophosphates and zinc diaryldithiophosphates.

Suitable antiwear agents include, for example, phosphates, phosphate esters, phosphites, thiophosphites, e.g. zinc dialkyl dithiophosphates, zinc diaryldithiophosphates, tricresyl phosphates, chlorinated waxes, sulphurised fats and olefins, such as thiodipropionic esters, dialkyl sulphides, dialkyl polysulphides, alkyl-mercaptopanes, dibenzothiophenes and 2,2'-dithiobis(benzothiazole); organic lead compounds, fatty acids, molybdenum complexes, 25 such as molybdenum disulphide, halogen substituted organosilicon compounds, organic silicon compounds, borates and halogen-substituted phosphorus compounds.

As specific examples of suitable detergents, the following should be mentioned: sulphonates, aromatic sulphonic acids, which are substituted with alkyl having a long 30 chain, phosphonates, thiophosphonates, phonolates, metal salts of alkylphenols, and alkyl sulphides.

Typical defoaming agents include silicon oils, e.g. dimethylpolysiloxane and organic silicon compounds such as diethyl silicates.

Organic acids, amines, phosphates, alcohols, sulphonates and phosphites are examples of 35

corrosion inhibitors.

The esters according to the invention are prepared by a conventional esterification reaction wherein a polyol or a mixture of polyols is (are) reacted with an acid mixture in the presence of a catalyst or without a catalyst. Various acids, such as sulphuric acid, hydrochloric acid, p-toluene sulphonic acid, butyl titanate, tin oxide etc., are suitable catalysts for carrying out the invention. A particularly advantageous catalyst is tin oxide.

During the reaction, the polyol is reacted with the acid component by using an equivalent amount of acid, a deficient amount of acid or a surplus of acid; the excess acid amounts to typically a maximum of 10 mol-%, preferably about 0.1 to 5 mol-%, in particular about 1 mol-%. The reaction temperature is 150 to 230 °C, preferably 170 to 220 °C and in particular about 190 to 210 °C.

The esterification can be carried out as a batch or semibatch process for example by adding the remaining acid later on. The most typical embodiment comprises carrying out esterification in the melt phase but it is also possible to use a hydrocarbon-type medium, such as toluene or xylene. The product is neutralized either with conventional bases (NaOH, NaHCO₃, Na₂CO₃ etc.) or with organic amines and are then washed. The degree of purification of the ester product is preferably over 85 %, in particular over 90 % and the acid number of the ester is preferably below 0.1 mg KOH/g.

The following examples illustrate the invention. They do not, however, limit the scope of the invention.

Example 1

Determination of ester solubility

Solubility in fluorinated hydrocarbons was determined as follows: 1 ml of the studied ester was put into a test tube which was closed with a stopper. The test tube was placed in a cold bath at a temperature of -30 °C. When the temperature of the test tube and the ester had reached -30 °C (after about 5 minutes), a fluorinated refrigerant, such as R-134a, was added to make a total volume of 10 ml.

The ester-refrigerant mixture was allowed to stand in the bath at -30 °C with possibly a light occasional stirring. After about 15 minutes the mixture was visually assessed and it

was determined whether the mixture contained one or two phases. If the ester and the refrigerant liquid formed one phase, the ester is completely dissolved in the refrigerant liquid. If there are two phases present in the mixture, the ester is either partially or completely insoluble in the refrigerant liquid.

5

Example 2

Preparation of esters of HPHP

The preparation of esters of HPHP is described in the following using the esters of HPHP and heptanoic acid as an example.

The raw materials were weighed into a glass bulb according to the following recipe: HPHP 50 g and heptanoic acid 64.6 g. The catalyst used comprised 0.17 g tinoxide. The esterification was carried out by stirring using a mixer with an electric motor and by

15 nitrigating the reaction mixture at about 210 °C. The reaction was complete within 7 hours.

Tinoxide was removed by filtration. Excess acid was neutralized from the reaction mixture with 2 - 5 wt-% triethylamine. The neutralization was carried out at 80 °C for 3 hours.

Warm water (2 - 5 wt-%) was added to the reaction mixture and it was mixed cautiously.

20 The solvent of the reaction mixture comprised heptane. Any formed aminocarboxylic acid salt or complex was separated. The solvent and the unreacted triethylamine were removed by vacuum distillation. The end product was filtered. The results are summarized in Table 1.

25

Table 1. Polyol esters of HPHP

| Sample | Polyol | Acids (mol-%) | V_{40} | V_{100} | VI | PP(°C) | Solubility in | |
|--------|--------|-------------------------|----------|-----------|-----|--------|---------------|-----------|
| | | | | | | | R-134a | |
| | | | | | | | -30 °C | -50 °C |
| 1 | HPHP | Heptanoic acid (100) | 11.63 | 2.98 | 111 | - | Excellent | Excellent |

30

Example 3**Preparation of esters of HPHP from acyclic anhydrides**

The preparation of esters of HPHP is illustrated by using the preparation of an ester of

5 HPHP and isobutyric anhydride as an example.

The raw materials were weighed into a glass reactor according to the following recipe:
 HPHP 17.5 g and isobutyric anhydride 19.36 g. The catalyst used comprised 0.37 g
 methanesulphonic acid. The esterification was carried out by adding the anhydride and the
 10 catalyst from a dropping funnel to the HPHP during 2 hours, and then the reaction mixture
 was stirred at about 150 °C for 2 hours.

Excess acid was neutralized from the reaction mixture and the catalyst was washed in a
 separation funnel with 3 x 25 ml 5 % sodium carbonate solution and 3 x 25 ml water. Any
 15 sodium salt or complex of the carboxylic acid were separated. Finally, the product was
 dried on sodium sulphate and filtered. Other esters were prepared by suitable modification
 of the conditions. The results are summarized in Table 2.

Table 2. Acid anhydride esters of HPHP

| Sample | Polyol | Acids (mol-%) | V ₄₀ | V ₁₀₀ | VI | Solubility in R-134a | |
|--------|--------|------------------------------|-----------------|------------------|----|-------------------------|-----------|
| | | | | | | -30 °C | -50 °C |
| 2 | HPHP | Isobutyric anhydride | 7.44 | 2.14 | 82 | Excellent | |
| 3 | HPHP | 2-ethylbutanoic anhydride | 11.84 | 2.79 | 64 | Excellent | Excellent |

Example 4**Preparation of complex esters of HPHP**

Complex esters of HPHP is described using the ester of HPHP, octanoic acid and adipic
 ester as an example.

The raw materials were weighed into a glass reactor according to the following recipe:
 HPHP 100 g, octanoic acid 94.8 g and adipic acid 24.0 g. The catalyst used comprised

0.328 g tin oxide, acid. The esterification was carried out by stirring and nitrigating the reaction mixture at about 210 °C. The reaction was complete within 7 hours.

Excess acid was neutralized from the reaction mixture with 5 wt-% triethylamine. The
 5 neutralization was carried out at 80 °C for 3 hours. Warm water (5 wt-%) was added to the reaction mixture and it was mixed cautiously. Any formed aminocarboxylic acid salt or complex was separated. The reaction mixture was then washed with a dilute mineral acid (1 molar H₃PO₄) and subsequently 1 to 2 times with warm water. Finally, the product was dried on sodium sulphate and filtered. Other esters were prepared by suitable modification
 10 of the conditions. The results are summarized in Table 3.

Table 3. Complex esters of HPHP

| 15 | Sample | Polyol | Acids (mol-%) | V ₄₀ | V ₁₀₀ | VI | PP(°C) | Solubility in R-134a | |
|----|--------|--------|--------------------------------|-----------------|------------------|-----|--------|-------------------------|-----------|
| | | | | -30 °C | -50 °C | | | | |
| | 4 | HPHP | C ₈ (80) AA (20) | 39.8 | 7.06 | 140 | -51 | Good | |
| | 5 | HPHP | C ₈ (80) SA (20) | 50.5 | 8.75 | 154 | -51 | Excellent | Excellent |

A_A = adipic acid

SA = sebasic acid

C₈ = octanoic acid

Example 5

Preparation of polyol/complex esters of HPHP

25

Following the process of Example 4 complex esters of mixtures of HPHP and some other polyols were prepared. The results are indicated in Table 4.

Table 4. Polyol/complex esters of HPHP

| 5 | Sample | Polyol | Acids (mol-%) | V ₄₀ | V ₁₀₀ | VI | PP(°C) | Solubility in R-134a | |
|----|--------|------------------------|--------------------------------|-----------------|------------------|-----|--------|-------------------------|-----------|
| | | | | | | | | -30 °C | -50 °C |
| | 6 | HPHP (60) BEPD (40) | C ₈ (90) AA (10) | 19.78 | 4.32 | 128 | -63 | Fair | |
| | 7 | HPHP (60) BEPD (40) | C ₈ (80) AA (20) | 33.20 | 6.15 | 136 | -54 | Good | |
| | 8 | HPHP (90) BEPD (10) | C ₈ (90) AA (10) | 21.57 | 4.61 | 133 | -60 | Excellent | Excellent |
| | 9 | HPHP (60) NPG (40) | C ₈ (80) AA (20) | 23.69 | 5.06 | 147 | -63 | Excellent | |
| 10 | 10 | HPHP (90) BEPD (10) | C ₈ (80) AA (20) | 32.83 | 6.14 | 137 | -60 | Excellent | |

BEPD = 2-butyl-2-ethyl-1,3-propanediol, NPG = neopentylglycol

15-06-1999

12

Claims:

1. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and
 - an ester of trimethylol propane, trimethylol ethane, pentaerythritol or 2,2,4-trimethylpentadiol, the amount of the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate being at least 50 mol-% of the polyol residue of the ester mixture,
 - an ester of 2-butyl-2-ethyl-1,3-propanediol, the molar ratio of the 2-butyl-2-ethyl-1,3-propanediol and the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate being 5:95 - 99:1, or
 - a polyol ester of neopentylglycol, 2-ethyl-1,3-hexanediol or 1,4-dimethylol-cyclohexane.
2. The refrigerant composition according to claim 1, wherein the polyol ester mixture is prepared *in situ*.
3. The refrigerant composition according to claim 1 or claim 2, wherein the carboxylic acid residue of the polyol ester is derived from a linear or branched C₄...C₁₈-carboxylic acid, or an anhydrides thereof, or it is derived from a mixture of linear or branched C₄...C₁₈-carboxylic acids or anhydrides thereof.
4. The refrigerant composition according to claim 3, wherein the carboxylic acid residue is derived from 2-ethylhexanoic acid, heptanoic acid, octanoic acid and/or lauric acid.
5. The refrigerant composition according to claim 1, wherein the carboxylic acid residue of the ester is derived from a mixture of mono- and dibasic carboxylic acids.
6. The refrigerant composition according to claim 5, wherein the monobasic carboxylic acid residue is derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or mixtures thereof.
7. The refrigerant composition according to claim 5 or claim 6, wherein the dibasic carboxylic acid residue is derived from oxalic acid, malonic acid, dimethylmalonic acid,

succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.

- 5 8. The refrigerant composition according to any of claims 5 to 7, wherein the molar ratio between the mono- and dibasic carboxylic acids is 50:50 to 95:5.
9. The refrigerant composition according to any of the preceding claims, wherein the fluorinated hydrocarbon based refrigerant is hydrofluorocarbon 134, hydrofluorocarbon
10 134a, hydrofluorocarbon 143, hydrofluorocarbon 143a, hydrofluorocarbon 152 or hydrofluorocarbon 152a or a mixture of hydrofluorocarbons.
- 10 15 10. Complex esters of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate which contain residues of both mono- and dibasic carboxylic acids, the molar ratio between the mono- and dibasic carboxylic acid residues in the ester being 50:50 to 95:5.
11. The complex esters according to claim 10, wherein the monobasic carboxylic acid residues are derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or mixtures thereof.
- 20 12. The complex esters according to claim 10 or claim 11, wherein the dibasic carboxylic acid residues are derived from oxalic acid, malonic acid, dimethyl malonic acid, succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.
- 25 13. The complex esters according to any of claims 16 to 19, mixed with esters and/or complex esters of another polyol.
- 30 14. The complex esters according to claim 13, wherein the esters are in a mixture of esters and/or complex esters of NPG or BEPD.
15. The use of an ester according to any of claims 10 to 14 as base oils for lubricants.

JULY 31 1998

BIRCH, STEWART, KOLASCH & BIRCH, LLP

COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO.

365-428P

FOR PATENT AND DESIGN APPLICATIONS

PLEASE NOTE:
YOU MUST
COMPLETE THE
FOLLOWING:

Insert Title: ➔

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Polyol and complex esters for use with, in particular,
 fluorinated refrigerants

Fill in Appropriate
 Information -
 For Use Without
 Specification
 Attached:

the specification of which is attached hereto. If not attached hereto,

the specification was filed on _____ as
 United States Application Number _____; and /or

the specification was filed on April 14, 1998 as PCT
 International Application Number PCT/FI98/00329; and was
 amended under PCT Article 19 on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

| Prior Foreign Application(s) | | | Priority Claimed |
|------------------------------|-----------|------------------------|---|
| 971548 ✓ | Finland | April 11, 1997 ✓ | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| (Number) | (Country) | (Month/Day/Year Filed) | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| 971549 ✓ | Finland | April 11, 1997 ✓ | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| (Number) | (Country) | (Month/Day/Year Filed) | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| 980730 ✓ | Finland | March 31, 1998 ✓ | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| (Number) | (Country) | (Month/Day/Year Filed) | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| (Number) | (Country) | (Month/Day/Year Filed) | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| (Number) | (Country) | (Month/Day/Year Filed) | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| (Number) | (Country) | (Month/Day/Year Filed) | <input type="checkbox"/> Yes <input type="checkbox"/> No |

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

Insert Provisional
 Application(s):
 (if any)

| | |
|----------------------|---------------|
| (Application Number) | (Filing Date) |
| (Application Number) | (Filing Date) |

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More Than 12 Months (6 Months for Designs) Prior To The Filing Date of This Application:

Insert Requested
 Information:
 (if appropriate)

| Country | Application No. | Date of Filing (Month/Day/Year) |
|---------|-----------------|---------------------------------|
| | | |

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Insert Prior U.S.
 Application(s):
 (if any)

| | | |
|----------------------|---------------|---|
| (Application Number) | (Filing Date) | (Status - patented, pending, abandoned) |
| (Application Number) | (Filing Date) | (Status - patented, pending, abandoned) |

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

| | |
|--|--|
| Terrell C. Birch (Reg. No. 19,382) | Raymond C. Stewart (Reg. No. 21,066) |
| Joseph A. Kolasch (Reg. No. 22,463) | James M. Slattery (Reg. No. 28,380) |
| Bernard L. Sweeney (Reg. No. 24,448) | Michael K. Mutter (Reg. No. 29,680) |
| Charles Gorenstein (Reg. No. 29,271) | Gerald M. Murphy, Jr. (Reg. No. 28,977) |
| Leonard R. Svensson (Reg. No. 30,330) | Terry L. Clark (Reg. No. 32,644) |
| Andrew D. Meikle (Reg. No. 32,868) | Marc S. Weiner (Reg. No. 32,181) |
| Joe McKinney Muncy (Reg. No. 32,334) | Donald J. Daley (Reg. No. 34,313) |
| C. Joseph Faraci (Reg. No. 32,350) | |

15 -
Send Correspondence to:

BIRCH, STEWART, KOLASCH & BIRCH, LLP

P.O. Box 747 • Falls Church, Virginia 22040-0747

Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

PLEASE NOTE:
YOU MUST
COMPLETE THE
FOLLOWING:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of First or Sole Inventor:
Insert Name of Inventor
Insert Date This Document is Signed

Insert Residence
Insert Citizenship

Insert Post Office Address

Full Name of Second Inventor, if any:
see above

Full Name of Third Inventor, if any:
see above

Full Name of Fourth Inventor, if any:
see above

Full Name of Fifth Inventor, if any:
see above

| | | | |
|--|------------------------------------|--------------------------|-----------------------------|
| GIVEN NAME <u>Jari</u> | FAMILY NAME <u>Koistinen</u> | INVENTOR'S SIGNATURE | DATE* September 20, 1999 |
| Residence (City, State & Country) <u>Jyväskylä, Finland</u> | | CITIZENSHIP Finnish | |
| POST OFFICE ADDRESS (Complete Street Address including City, State & Country) <u>Lamminmutka 2 C 14, FIN-40520 Jyväskylä, Finland</u> | | | |
| GIVEN NAME <u>Kari</u> | FAMILY NAME <u>Rissanen</u> | INVENTOR'S SIGNATURE | DATE* September 20, 1999 |
| Residence (City, State & Country) <u>Hankasalmi, Finland</u> | | CITIZENSHIP Finnish | |
| POST OFFICE ADDRESS (Complete Street Address including City, State & Country) <u>Hankamäentie 13, FIN-41520 Hankasalmi, Finland</u> | | | |
| GIVEN NAME <u>Laura</u> | FAMILY NAME <u>Silvennoinen</u> | INVENTOR'S SIGNATURE | DATE* September 20, 1999 |
| Residence (City, State & Country) <u>Jyväskylä, Finland</u> | | CITIZENSHIP Finnish | |
| POST OFFICE ADDRESS (Complete Street Address including City, State & Country) <u>Kilpisenkatu 16 A 20, FIN-40100 Jyväskylä, Finland</u> | | | |
| GIVEN NAME <u>Salme</u> | FAMILY NAME <u>Koskimies</u> | INVENTOR'S SIGNATURE | DATE* September 20, 1999 |
| Residence (City, State & Country) <u>Helsinki, Finland</u> | | CITIZENSHIP Finnish | |
| POST OFFICE ADDRESS (Complete Street Address including City, State & Country) <u>Hämeenapajantie 7, FIN-00850 Helsinki, Finland</u> | | | |
| GIVEN NAME | FAMILY NAME | INVENTOR'S SIGNATURE | DATE* |
| Residence (City, State & Country) | | CITIZENSHIP | |
| POST OFFICE ADDRESS (Complete Street Address including City, State & Country) | | | |

* DATE OF SIGNATURE